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(CONTRIBUTION FROM THE CHEMICAL LABORATORY
OF THE UNIVERSITY OF KANSAS)

The Preparation of a Solid Rhenide¹

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(1) Constructed from a thesis submitted by Justo B. Bravo in partial fulfillment of the requirements for the degree of Doctor of Philosophy, January, 1953.

By JUSTO B. BRAVO, ERNEST GRISWOLD AND JACOB KLEINBERG

Abstract

The reduction of potassium perrhenate in ethylenediamine-water solutions by means of potassium metal yields a white solid containing uninegative rhenium (rhenide) mixed with potassium hydroxide. Under optimum conditions of reduction an apparent conversion of up to 90% of the perrhenate to solid rhenide is obtained.

A number of extractions of the solid with isopropyl alcohol results in the removal of a large proportion of the potassium hydroxide and in the formation of a colloidal brown liquid which contains potassium hydroxide, isopropyl alcohol, and rhenium, the latter almost entirely in the uninegative state. Fractional extraction of this brown liquid finally gives a gray solid usually containing between 55 - 60% rhenium, all as potassium rhenide.

Analysis of the gray solid shows the presence of small amounts (about 5%) of potassium hydroxide as impurity and also the presence of approximately four molecules of water per rhenide ion. Magnetic measurements demonstrate that the rhenide compound is slightly paramagnetic, the degree of paramagnetism being even less than that re-

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quired for a substance with one unpaired electron. Inasmuch as the rhenium atom possesses five unpaired electrons, the magnetic evidence indicates that the formation of the rhenide ion involves a considerable modification in electronic configuration. The magnetic data do not distinguish between two alternative structures; one in which the rhenide ion has a halide configuration, and the other in which the rhenium exists in a hydrated complex having four water molecules coordinated at the corners of a square. From energy considerations the latter structure appears to be the more plausible.

The discovery by Lundell and Knowles² in 1937 of the existence

(2) G.E.P. Lundell and H.B. Knowles, J. Research Nat. Bur. Standards, 18, 629(1937).

of uninegative rhenium (rhenide) has been confirmed by other investigators;³⁻⁶ up to the present, however, no solid substance containing

(3) O. Tomiček and F. Tomiček, Collection Czech. Chem. Commun., 11 626(1939).

(4) (a) J.J. Lingane, THIS JOURNAL, 64, 1001(1942); (b) ibid., 64, 2162(1942).

(5) E.K. Maun and N. Davidson, ibid., 72, 3509(1950).

(6) C.L. Rulfs and P.J. Elving, ibid., 73, 3287(1951).

the rhenide ion has been prepared. In a preliminary communication from this Laboratory⁷ the production for the first time of a solid

(7) E. Griswold, J. Kleinberg, and J. B. Bravo, Science, 115, 376 (1952).

rhenide material in admixture with potassium hydroxide was reported. The current communication describes the preparation and some properties of potassium rhenide tetrahydrate, which has been obtained in greater than 90 per cent purity. This compound was extracted from a mixture consisting essentially of potassium rhenide and potassium hydroxide, which had been prepared by the reduction of potassium perrhenate in ethylenediamine-water solutions by means of potassium metal.

The Reduction of Potassium Perrhenate

Materials. - Potassium perrhenate obtained from the University of Tennessee and of 99.8% purity was used without further purification. The potassium sticks were obtained from Baker and Adamson. The ethylenediamine employed was of Eastman Kodak Co. white label quality. The water content of this material was determined by titration with Karl Fischer reagent,⁸ which was purchased with the water-in-methanol

(8) J. Mitchell and D.M. Smith, Aquametry: Application of the Karl Fischer Reagent to Quantitative Analysis Involving Water, Interscience Publishers, Inc., New York, 1948.

standard from Hartman-Leddin Co. Spent ethylenediamine was recovered by distillation from potassium hydroxide sticks. Anhydrous ethyl ether was produced by drying special drum ether from Carbide and Carbon Chemicals over sodium.

The Reduction Procedure. - The apparatus employed for the reduction of potassium perrhenate is shown in Fig.1. The reaction chamber was about 3.5 cm. in diameter and approximately 15 cm. high. Sampling bulbs A and B were inserted in the reaction chamber through

ground glass joints. The nitrogen delivery tube extended close to the bottom of the reaction chamber in order that the gas would have a stirring effect on the reaction mixture. The presence at C of a large standard taper joint permitted the removal of the lower part of the reaction chamber for sampling purposes. An ultrafine fritted glass disk sealed into the bottom of the reaction chamber served, after removal of the solvent into the filter trap by means of an aspirator, to hold the insoluble white product formed in the reduction reaction.

Prior to each reduction the several pieces of the reaction chamber assembly were cleaned and dried in an oven at 110° . The apparatus was then assembled except for the sampling bulbs. The openings for the bulbs were stoppered with standard taper plugs and dry, oxygen-free nitrogen was passed through the system for at least 10 min. to sweep out the air. The sampling bulb A was then charged with a weighed quantity (2 or 4 g.) of potassium, which had been cut and weighed under benzene. Bulb B was charged with 50 or 100 ml. of 3mM potassium perrhenate solution in ethylenediamine-water solution containing 9.8% water. After the sampling bulbs had been connected with the reaction chamber, bulb A was rotated and the potassium metal dropped into the chamber. This was followed by the introduction of the perrhenate solution.

Usually from 2 to 10 min. was required for complete reaction of the potassium, during which time the temperature of the reaction mixture rose to about 70° C. When the reaction was complete, the white

solid product was filtered by aspiration and twice washed with anhydrous ethyl ether, being stirred at the same time. After a final rinse with ether the solid was dried thoroughly by means of a stream of dry, oxygen-free nitrogen and was then dissolved in distilled water and made up to volume. Separate aliquots of the solution were analyzed for rhenium content, and for reducing power in terms of the number of g. equivalents of standard oxidizing agent required to oxidize 1 g. atom of rhenium to the perrhenate state.

Analytical Methods. - The reducing power of the rhenium was determined by the addition of an aliquot of the solution described above to a measured quantity of an excess of standard dichromate solution in a considerable excess of 4 N sulfuric acid; a measured quantity of standard iron(II) sulfate was then added, and the excess iron(II) sulfate was titrated with standard dichromate in the presence of diphenylamine sulfonic acid indicator. A suitable correction was made for reaction of the indicator with the dichromate.⁹

(9) I.M. Kolthoff and E.B. Sandell, Textbook of Quantitative Inorganic Analysis, The MacMillan Co., New York, 1947, pp. 493-494.

Rhenium was determined in the following manner. An aliquot of the solution was digested with 2 ml. of 30% hydrogen peroxide and sufficient 1:1 hydrochloric acid to make the final solution acidic. Digestion was continued until excess hydrogen peroxide had been destroyed. The perrhenate formed was then converted to $\text{ReO}(\text{CNS})_4$ by treatment with potassium thiocyanate and tin(II) chloride, and the oxythiocyanate determined spectrophotometrically as described by

Sandell.¹⁰ A Model DU Beckman spectrophotometer was employed.

(10) E.B. Sandell, Colorimetric Determination of Traces of Metals, Interscience Publishers, Inc., New York, 1944, pp. 375-383.

Results. - The results of typical reduction experiments are summarized in Table I. It should be emphasized that the conditions of reduction as listed in the table are those which, after many preliminary experiments, were found to give excellent conversions of perrhenate to rhenide. It is seen that under optimum conditions up to 90% of the initial perrhenate apparently is converted to solid rhenide. The solid mixture of potassium hydroxide and rhenide which is formed contains about 0.5% rhenium. In almost every case, the filtrate possessed some reducing power, indicating that it also contained rhenide.

It is questionable that potassium metal itself is the actual reducing agent. The reaction of the metal with the water present in the ethylenediamine gives rise to hydrogen, and it is possible that this is the agent responsible for the reduction of the perrhenate.

The Separation of Potassium Rhenide

Preliminary Experiments. - Exploratory efforts to extract potassium hydroxide from the solid mixture produced by reduction of perrhenate demonstrated that, of the various solvents tested (liquid ammonia, ethyl alcohol, dioxane, cellosolve, n-amyl alcohol, n-butyl alcohol, and isopropyl alcohol), isopropyl alcohol was the most satisfactory. This solvent dissolves potassium hydroxide and has

Table I

Reduction of Potassium Perrhenate by Potassium
in Ethylenediamine-Water Solution
(Concentration of KReO_4 , 3mM; 9.8% H_2O)

<u>Millimoles of rhenium titrated</u>	<u>Ml. of 0.1 N $\text{K}_2\text{Cr}_2\text{O}_7$ re-</u> <u>quired</u>	<u>Valence no. change; theo-</u> <u>retical, S</u>	<u>Total rhen-</u> <u>ium in solid,</u> <u>mg.</u>	<u>Conver-</u> <u>sion to</u> <u>rhenide, %</u>
0.0376	3.00	7.99	8.40	30.0 ^{a,c}
.0311	2.48	7.97	6.96	24.9 ^{a,c}
.0365	2.89	7.92	8.16	29.2 ^{a,c}
.0174	1.39	7.97	5.02	18.0 ^{a,c}
.0651	5.32	8.16	14.50	52.0 ^a
.0681	5.33	7.82	15.26	54.7 ^a
.1014	8.44	8.30	37.80	67.6 ^b
.1356	11.02	8.13	50.50	90.4 ^b
.1390	11.38	8.18	51.76	92.5 ^b

^a Fifty milliliters of perrhenate sample and 2.00(± 0.05) g. of potassium were used in these experiments.

^b One hundred milliliters of perrhenate sample and 4.00(± 0.05) g. of potassium were used in these experiments.

^c Initial reaction temperature 15° C.; all other experiments were carried out at an initial temperature of about 25° C.

practically no solvent action on the rhenide. However, in the course of treatment of the mixture with isopropyl alcohol two liquid layers are formed. The upper colorless layer, formed in greater volume, contains much potassium hydroxide but no rhenide. The lower layer, brown in color and colloidal in nature, contains potassium hydroxide and all of the rhenium.¹¹ Further extractions of this brown liquid

(11) Occasionally a small amount of white solid remained when the two layers were formed. The white solid was combined with the lower brown layer and the mixture further extracted as described for the brown layer alone.

with isopropyl alcohol, continued until the brown layer has almost disappeared, yield a grayish white solid containing in most cases, approximately 20% of rhenium, nearly all of which is apparently in the uninegative state.

In an effort to concentrate the rhenide further, the grayish white solid was subjected to further extractions with isopropyl alcohol. In most of these experiments the solid became darker, and although its rhenium content increased, the reducing power was found to have undergone some diminution. This fact, indicating oxidation of part of the rhenium during extraction, suggested that the brown liquid layer might contain some unreduced perrhenate, which appears in the grayish white solid obtained by complete extraction of the brown layer, and, with decrease in concentration of hydroxide during further extraction of the solid, interacts with the rhenide to form metallic rhenium.

In order to test this hypothesis, a series of fractional extractions of the brown liquid layer were carried out. The procedure employed was as follows, all operations involving transfer being carried out in a dry box.

Two reductions were performed as previously described, each with 100 ml. of $3mM$ potassium perrhenate solution in ethylenediamine-water mixture containing 10.8% water; $6.00(\pm 0.05)$ g. of potassium was used as reducing agent and the reaction was carried out at an initial temperature of about $25^{\circ} C$.

The white solid products from these reductions were transferred to a single 60-ml. glass stoppered centrifuge tube. The tube was filled with oxygen-free anhydrous isopropyl alcohol (obtained by the fractionation from sodium of 98% Baker and Adamson material in a nitrogen atmosphere) and then shaken on a mechanical shaker for 1 hr. After centrifugation, the alcoholic extract was discarded. A total of three extractions usually resulted in the formation of the two layers previously described. The brown layer (plus any white solid which may have been present) was extracted once with isopropyl alcohol. Invariably there appeared at this stage a small amount of white solid. The clear alcohol layer was drained off and the brown layer was separated by decantation to another 60-ml. glass stoppered centrifuge tube. The solid phase was extracted once again with the alcohol, washed with anhydrous ether, and dried in a stream of nitrogen. The rhenium content and reducing power were then determined as previously described, except that the solid was dissolved

in 10% potassium hydroxide solution rather than in distilled water. The results of typical experiments are given in the rows marked A in Table II.

The brown liquid phase was subjected to three additional extractions with isopropyl alcohol, each of which gave a deposit of a gray solid. The small amount of brown liquid still remaining was drained off, and the solid which had been deposited was extracted once again, washed with ether, dried, and analyzed after dissolution in 10% potassium hydroxide solution. The results appear in the rows labeled B in Table II.

The results shown in Table II are in agreement with the hypothesis that a small amount of unreduced perrhenate is present in the original brown layer. The perrhenate apparently is thrown out in the first small amount of solid deposit when the brown layer is treated with isopropyl alcohol, so that all of the remaining rhenium is in the uninegative state.

The Isolation of Potassium Rhenide Tetrahydrate. - A series of experiments was performed to determine the maximum rhenide content obtainable in the solid. The gray solid material, which had been freed of perrhenate by the method just described, was further extracted with isopropyl alcohol until two successive extracts (each the product of one hour's treatment) gave no test for potassium hydroxide. Approximately twenty extractions were required. Prior to each extraction, after the fifth one, the solid was crushed and stirred with a glass rod. The solid was finally washed with ether, dried, and analyzed for rhenium content and reducing power. The data

Table II

Fractional Extraction of Rhenide-Potassium Hydroxide
Brown Liquid Phases^a

Expt. no.		Weight of solid, mg.	Total rhenium content, mg.	% Rhenium	Valence no. change; theo- retical, 8
1	A	22.7	11.7	51.5	3.85
	B	86.2	48.8	56.6	8.16
2	A	15.6	8.1	52.0	5.42
	B	157.1	70.5	44.8	7.72
3	A	18.7	8.5	45.4	6.56
	B	146.7	79.0	53.8	8.17
4	A	15.2	8.9	58.7	5.62
	B	162.7	76.0	46.8	8.14
5	A	39.9	7.9	19.7	6.16
	B	147.4	77.1	52.4	8.02
6	A	15.2	7.1	46.7	5.47
	B	190.9	85.3	44.7	8.00

^a The original reductions were carried out with 100 ml. of 3mM $KReO_4$ solution in ethylenediamine-water mixture containing 10.8 % water; 6.00(+ 0.05) g. of potassium was used as reducing agent. Each extraction experiment was performed on two batches of reduction product.

obtained from these experiments are given in Table III. It is seen that the maximum rhenium content of the solid approximates 61 %. It should be pointed out that the solids analyzed still contained small amounts of potassium hydroxide, as evidenced by the fact that long contact (about 10 hrs.) with isopropyl alcohol resulted in additional extraction of base.

Portions of two of the solids (see Table III) were analyzed for carbon, nitrogen, and hydrogen.¹² The amounts of carbon and nitrogen

(12) Sample no. 5, Table III, was analyzed by Dr. G. Weiler and Dr. F.B. Strauss, Microanalytical Laboratory, Oxford, Engl, and sample no. 8 by Micro-Tech Laboratories, Skokie, Ill.

were found to be insignificant, whereas the hydrogen contents, as is shown below, correspond closely to that calculated for a tetrahydrate.

<u>% Re</u>	<u>% H</u>	<u>Atomic ratio, H:Re</u>
57.7	2.50	8.0
54.6	2.33	8.0
	2.14	7.3

This result is entirely consistent with the fact that the maximum rhenium content found in the extracted solid was 61.5 %, the theoretical value for the tetrahydrate being 62.6 %. It is somewhat surprising that, although it was prepared in a medium rich in the excellent coordinator ethylenediamine, the rhenide compound nevertheless combined preferentially with water molecules.

Additional samples of the rhenide compound were prepared, extracted as previously described, and analyzed for both rhenium and

Table III

The Separation of Rhenide from Admixture
with Potassium Hydroxide^a

Expt. no.	Weight of solid, mg.	Total rhenium content, mg.	% Rhenium	Valence no. change; theo- retical, 8
1	140.0	83.4	59.6	7.96
2	122.1	75.1	61.5	7.98
3	84.7	51.6	60.9	8.07
4	99.2	59.2	59.6	8.06
5	49.2 ^b	26.9	54.6	8.14
6	102.4	54.2	52.9	8.10
7	102.6	55.4	54.0	8.21
8	41.0 ^b	23.7	57.7	8.07

^a The original reductions were carried out under the identical conditions described in Table II. Each extraction experiment was performed on two batches of reduction product.

^b This does not represent the total quantity of solid obtained, a portion having been used for analysis for C, H, and N.

potassium.¹³ From the excess of potassium beyond that required for

(13) Potassium was determined by means of flame photometry, according to directions contained in the Instruction Manual, Flame Photometer, Model 52-C, The Perkin-Elmer Corp., Norwalk, Conn., 1952.

potassium rhenide formation, the percentage of potassium hydroxide present as impurity was calculated; the water content was obtained as the difference between the total quantity of material and the sum of the potassium rhenide and potassium hydroxide present. The results which are shown in Table IV, also definitely indicate that potassium rhenide is formed as a tetrahydrate. The actual percentages of water and the water:rhenium ratios are a little lower than those which appear in the table, since the small and variable (about 1-2 %) content of organic material, presumably ethylenediamine, has been neglected in the calculations.

Some Properties of Potassium Rhenide Tetrahydrate

Magnetic measurements by means of a Gouy balance demonstrate that the solid rhenide is slightly paramagnetic, giving values at 20° C. of 254×10^{-6} and 223×10^{-6} c.g.s. unit, respectively, for the molar susceptibility of $KRe \cdot 4H_2O$ in two different samples, after correction for the diamagnetism of the potassium hydroxide impurity. This degree of paramagnetism is even less than that (about 1300×10^{-6} c.g.s. unit) required for a substance with one unpaired electron. Inasmuch as the rhenium atom possesses five unpaired electrons, the magnetic evidence indicates that the formation of the rhenide ion

Table IV

Analysis of Potassium Rhenide^a

<u>% Rhenium</u>	<u>% Potassium</u>	<u>% Potassium hydroxide</u>	<u>% Water</u>	<u>H₂O:Re ratio</u>
58.4	17.8	7.9	21.4	3.8
55.8	16.8	7.0	25.5	4.7
57.2	15.6	5.1	25.6	4.6
57.9	15.5	4.8	25.1	4.5

^a The product was washed with anhydrous ether and treated with a stream of dry nitrogen.

complex having four water molecules coordinated at the corners of a square is consistent with energy considerations, and also with the magnetic data.¹⁶

- (16) In the Pauling structure, if the electrons of the water molecules are not considered, the electronic distribution may be considered to be C given above, but it must be recognized that only four 5d orbitals are available, rather than all five. The coordination of the rhenium with water molecules rather than with ethylenediamine is explained by Pauling (private communication) in the following manner: "I feel that there will be a very strong tendency for the rhenium atom to form covalent bonds. However, if the covalent bonds have too large an amount of covalent character there will be built up a very large negative charge on the rhenium atom, which would be contrary to the electroneutrality principle. [See J. Chem. Soc., 1948, 1461.] Accordingly the bonds to the four ligated atoms would be expected to have a rather large amount of ionic character, although still retaining a significant amount of covalent character. For this reason bonds to oxygen would be preferred in the rhenide complex over bonds to nitrogen, which, because of the smaller electronegativity of nitrogen, would be less stable, with a large amount of ionic character, than the bonds to oxygen. I think that this provides an explanation not only of the preference of the rhenide ion for water molecules, over ethylenediamine groups, but also for the ligation of only four water molecules, rather than six."
-

Although potassium rhenide tetrahydrate, as isolated, is gray in color, it is probable that the pure substance is actually colorless, inasmuch as the original reduction product, a mixture of rhenide and potassium hydroxide, is colorless. The gray color appears after extraction from the brown, colloidal dispersion in isopropyl alcohol, and probably is attributable to the adsorption of colloidal material. That this is a reasonable explanation is seen from the

fact that the compound dissolves in aqueous potassium hydroxide to give pale yellow solutions which exhibit the Tyndall effect.

Treatment of such solutions with aqueous thallium(I) nitrate gives a white precipitate which presumably is thallium(I) rhenide. Unfortunately the precipitate is unstable and soon is converted to a black substance which proved to be metallic thallium; perrhenate ion was identified in the solution.

Acknowledgement. The authors are indebted to the Office of Naval Research for financial support of this investigation.

Lawrence, Kansas

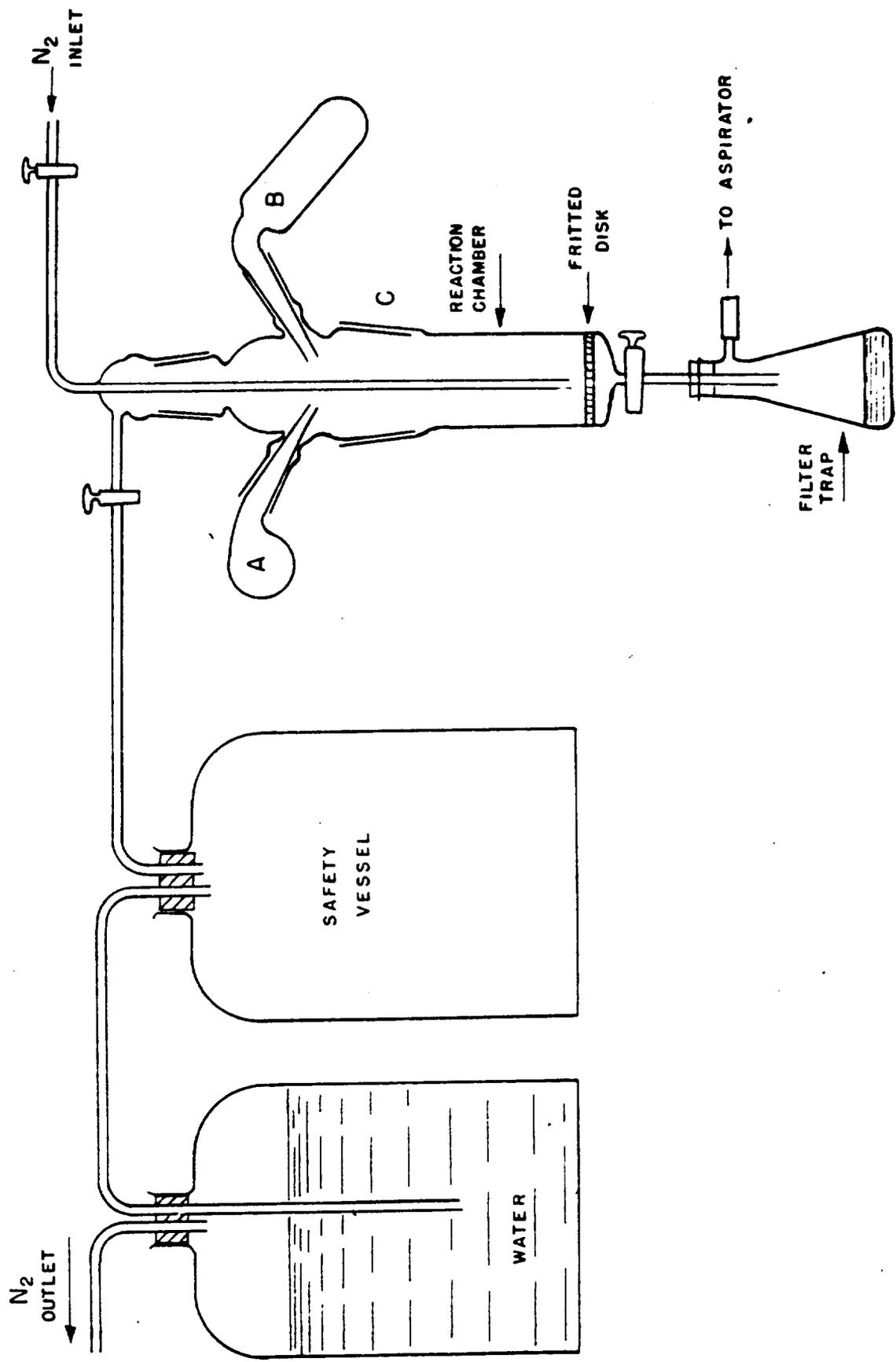


Figure 1 Apparatus for Reduction of Potassium Perrhenate Solution with Metallic Potassium.